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(54) **Title:** PROCESS FOR THE PREPARATION OF A LEVULINIC ACID DERIVED COMPOUND

(57) **Abstract:** The invention relates to a process for the preparation of a compound selected from the group consisting of levulinic acid ketals, gamma valerolactone, n- alkylpyrrolidones, pentandiols, pentanols, methyl tetra hydrofuran, delta amino levulinic acid, and succinic acid from a composition comprising levulinic acid and optionally a compound having a boiling temperature of less than 245°C said process comprising: subjecting the composition to distillation and recovering a residue comprising at least 1 wt% angelica lactone; subjecting the recovered residue to a chemical reaction step under conditions and time and temperature to produce the compound; and optionally isolating the compound. This process is simple and afford high yields.



WO 2014/087014 A1

PROCESS FOR THE PREPARATION OF A LEVULINIC ACID DERIVED COMPOUND

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Field of the invention

The present invention relates to a process for the preparation of a levulinic acid derived product and to the use of reactive distillation in a process for the preparation of such compound.

10

Background of the invention

Levulinic acid is a starting molecule for the synthesis of commercially important compounds. For example, levulinic acid can be used to produce levulinic acid ketals, gamma valerolactone, n-alkylpyrrolidones, pentandiols, pentanols, methyl tetra
15 hydrofuran, delta amino levulinic acid, and succinic acid. As in most reactions, levulinic acid as a reactant to make other compounds must be pure. Commonly used purification techniques include solvent-solvent extraction and distillation. Commercially, levulinic acid is made from furfuryl alcohol. When levulinic acid is producing from furfuryl alcohol, it can be isolated e.g. by distillation. It is also possible to produce levulinic acid
20 by acid hydrolysis of biomass although this is not commercially practiced. In addition to levulinic acid, biomass hydrolysates usually also contain low-boiling compounds such as formic acid, acetic acid, and proprionic acid. The inventors have surprisingly found that when such biomass hydrolysate is subjected to distillation in order to separate the levulinic acid from the biomass hydrolysate, the levulinic acid yield is unsatisfactory.
25 The inventors have tried hard to increase the yield of levulinic acid in the distillate, because low yields of levulinic acid after the distillation would mean that the yield, and therefore the economics of the production of levulinic acid esters would also be poor.

Summary of the invention

30

The invention provides an improved process for the preparation of a levulinic acid derived compound selected from the group consisting of levulinic acid ketals, gamma valerolactone, n-alkylpyrrolidones, pentandiols, pentanols, methyl tetra hydrofuran, delta amino levulinic acid, and succinic acid starting from a composition comprising levulinic acid and optionally a compound having a boiling temperature of

less than 245°C, wherein a distillation residue comprising angelica lactone is recovered and subjected to a chemical reaction step under conditions and time and temperature to produce the desired compound. The process is suitable for preparing levulinic acid from compositions made by acid hydrolysis of a lignocellulosic biomass, and also from
5 compositions made by acid hydrolysis of sugar such as glucose and fructose.

Detailed description of the invention

The invention provides a process for the preparation of a compound selected from the group consisting of levulinic acid ketals, gamma valerolactone, n-alkylpyrrolidones,
10 pentandriols, pentanols, methyl tetra hydrofuran, delta amino levulinic acid, and succinic acid from a composition comprising levulinic acid and optionally a compound having a boiling temperature of less than 245°C said process comprising:

- subjecting the composition to distillation and recovering a residue comprising at least 1 wt% angelica lactone;
- 15 - subjecting the recovered residue to a chemical reaction step under conditions and time and temperature to produce the compound; and optionally
- isolating the compound.

Throughout this specification "the compound" shall refer to a levulinic acid ketal, gamma valerolactone, n-alkylpyrrolidone, pentandiol, pentanol, methyl tetra hydrofuran,
20 delta amino levulinic acid, or succinic acid. Thus, the compound is a levulinic acid derived compound.

The inventors surprisingly found that when a biomass or C6 sugars hydrolysate is subjected to distillation in order to isolate levulinic acid, angelica lactone is formed during the distillation. The inventors have realized that levulinic acid derived
25 compounds can be efficiently produced from a biomass or C6 sugars hydrolysate by recovering a distillation residue comprising at least 1 wt% angelica lactone. The process of the invention is particularly advantageous when carried out as a batch process.

30 The boiling temperature is measured at standard conditions, namely at 1 atmosphere, or 760.00 mm Hg. At this pressure, the boiling temperature of pure water is 100°C, and the boiling point of levulinic acid is 245°C. The distillation preferably comprises reactive distillation. The distillation is preferably done under reactive conditions such that levulinic acid may be converted to angelica lactone. The distillation

temperature is preferably 80°C or more, more preferably between 120 and 150°C. The pressure is preferably 10 mbar or higher. Such pressures and temperatures may result in a distillation residue having at least 1 wt% angelica lactone. Preferably, during said distillation levulinic acid goes into the gas phase, where reactive distillation to angelica
5 lactone may take place, which may be recovered as a distillation residue. The compound having a boiling temperature of less than 245°C preferably has a boiling temperature of at least 90°C.

The composition may comprise formic acid, acetic acid, furfural, and/or propionic acid. That is, the compound having a boiling point of less than 245°C may comprise
10 formic acid, acetic acid, furfural, and/or propionic acid (i.e. may comprise each one of these compounds or a combination of two or more of these compounds).

The composition may comprise a biomass hydrolysate. Acid hydrolysis of biomass may not only result in formation of levulinic acid, but usually also results in the formation of formic acid, boiling temperature 100°C. Often a range of other low boiling
15 compounds are produced such as acetic acid, furfural, and propionic acid, all having a boiling temperature of 90°C or higher, but lower than the boiling temperature of levulinic acid. The biomass may be or may be derived from grass, cereal, starch, algae, tree bark, hay, straw, leaves, paper pulp, paper sludge, or dung. Paper pulp, or simply pulp, is a lignocellulosic fibrous material prepared by chemically or mechanically separating
20 cellulose from wood, fibre crops or waste paper. Pulp is rich in cellulose and other carbohydrates. Paper sludge, or simply sludge, is a lignocellulosic fibrous containing cellulose fibres too short for usage in the paper industry. The biomass may comprise lignocellulosic biomass. Lignocellulosic biomass typically has a fibrous nature and comprises a bran fraction that contains the majority of lignocellulosic (bran) fibers. As
25 an example, corn fiber is a heterogeneous complex of carbohydrate polymers and lignin. It is primarily composed of the outer kernel covering or seed pericarp, along with 10–25% adherent starch. Carbohydrate analyses of corn fiber vary considerably according to the source of the material. The lignocellulosic biomass may comprise hemicellulose.

30 In one embodiment, the composition is a biomass hydrolysate made by acid hydrolysis of lignocellulosic biomass.

In another embodiment, the composition is made by acid hydrolysis of C6 sugars, particularly of fructose or glucose or mixtures thereof. Sucrose ($C_{12}H_{22}O_{11}$) can be broken down into one molecule of glucose ($C_6H_{12}O_6$) plus one molecule of fructose

(also $C_6H_{12}O_6$, an isomer of glucose), in a weakly acidic environment by a process called inversion. Fructose can also be made by enzymatic isomerization of glucose. Sucrose is commonly produced from biomass such as beet, corn and cane.

The conditions for the acid hydrolysis of biomass or C6 sugars are such it results in the formation of at least levulinic acid and optionally a compound having a boiling temperature of less than 245°C and preferably also of tar and/or humins. Suitable acids include sulphuric acid, hydrochloric acid, and phosphoric acid. A preferred acid is sulphuric acid, preferably diluted sulphuric acid, for example at a concentration between 1.5 – 3%. The temperature in the acid hydrolysis may depend on the source of carbohydrates, and may range between 150-250°C, preferably between 170-240°C, more preferably between 190-230°C, even more preferably between 200 and 220°C. The acid hydrolysis may comprise one, two, or more stages. The pressure may also depend on the source of carbohydrates, as well as on the temperature, and may be anywhere between 1 and 50 bar, preferably between 5 and 40 bar, even more preferably between 10 and 30 bar. Suitable reactors include plugflow reactors, backmix reactors, and CSTR reactors. Different reactors for different stages may be used.

The distillation residue may comprise levulinic acid, i.e. it may be a mixture comprising at least 1 wt% angelica lactone and levulinic acid. The composition may be an aqueous liquid (e.g. solution or suspension). The composition may also comprise an organic liquid, such as e.g. an organic phase obtained by solvent-solvent extraction.

Liquid-liquid extraction is a process for separating components (the solutes) of a liquid (the feed) by contact with a second liquid phase (the solvent). The two liquids must not be completely mutually miscible. The process takes advantage of differences in the chemical properties of the feed components, such as differences in polarity and hydrophobic/hydrophilic character to separate them (T.C. Frank, L.Dahuron, B.S. Holden, W.D. Prince, A.F. Seibert, L.C. Wilson, Liquid-liquid extraction and other liquid-liquid operations and equipment in Perry's Chemical Engineering Handbook, 8th Edition, Section 15). Two streams result from the liquid-liquid extraction process: the extract, which is the solvent rich solution containing the desired extracted solute, and the raffinate, the residual feed solution containing little solute. Solvent extraction commonly (but not necessarily) takes place with an aqueous solution as one liquid and an organic solvent or mixture of solvents as the other. Numerous solvents with various properties are used in solvent extraction (Y.Marcus, Principles of Solubility and

Solutions, in J. Rydberg, M. Cox, C. Musicas, G.R. Chopin (Editors), Solvent Extraction Principles and Practice, 2nd Edition, Chapter 2, Marcel Dekker Inc., New York). Extraction capacity of a solvent can be adjusted by changing process parameters like temperature or pH.

5 Before subjecting the composition to the distillation to produce the distillation residue, the composition may undergo one or more additional steps, preferably non-chemical steps. Examples of such steps include concentration, e.g. by flashing, solvent-solvent extraction, solid/liquid separation. A combination of two or more of these steps is also possible. Suitable solid-liquid separation techniques include filtration
10 and centrifugation. A flashing step may combine cooling of a biomass hydrolysate after acid hydrolysis and concentration of such biomass.

 The amount of angelica lactone on the residue is at least 1 wt% relative to the total weight of the residue. Preferably the amount is at least 2%, at least 5%, at least 10%, more preferably at least 15%, at least 20%, more preferably at least 30%, at least
15 40%, even more preferably at least 50%, at least 60%, even more preferably at least 70%, at least 80%, or at least 90%, even more preferably at least 95 wt%.

 The composition comprising levulinic acid and optionally a compound having a boiling point of less than 245°C may further comprise humins, tar, and/or char. Tar and char represent organic material which is insoluble in water, which is dark in colour and
20 which tends to become viscous and very dark to almost black when concentrated. Tar can be formed during heating of organic material, for example by pyrolysis, but is also formed when carbohydrates are subjected to acid hydrolysis, particularly when done at high temperatures. Char usually refers to solid material, for example the remains of solid biomass that has been incompletely combusted, such as charcoal if wood is
25 incompletely burned. Tar usually refers (viscous) liquid, e.g. derived from the destructive distillation of organic matter.

 Humins may also be produced by acid hydrolysis of carbohydrates. Yang and Sen (Chem. Sus. Chem. 2010, vol. 3, 597-603) report the formation of humins during production of fuels from carbohydrates such as fructose. They speculate that the
30 humins are formed by acid-catalyzed dehydration. According to US7,896,944 the molecular weight of humins ranges from 2.5 to 300 kDa. In the context of the invention, "char" is understood to include "tar". The presence of tar is undesired, amongst other reasons because it may stick to the wall of a reactor. It may also cause problems in a distillation. If a distillation process consists of more than one unit, which is often the

case, any char present in the feed of a distillation char may accumulate in later distillation units and will be even more viscous and darkly-coloured, and will also be more concentrated in the bottom, because products exit the “train” via the top sections.

Before subjecting the distillation residue to the chemical reaction to produce the compound, the recovered residue may undergo one or more additional steps, preferably non-chemical steps. Examples of such steps include concentration, e.g. by flashing, solvent-solvent extraction, solid/liquid separation, and/or distillation. A combination of two or more of these steps is also possible.

Therefore, the invention also provides a process for the preparation of a compound selected from the group consisting of levulinic acid ketals, gamma valerolactone, n-alkylpyrrolidones, pentandriols, pentanols, methyl tetra hydrofuran, delta amino levulinic acid, and succinic acid from a biomass hydrolysate comprising levulinic acid, and optionally a compound having a boiling temperature of less than 245°C, said process comprising :

- optionally subjecting said biomass hydrolysate to a solid-liquid separation to yield a solid fraction and a liquid fraction and collecting said liquid fraction;
- optionally subjecting said biomass hydrolysate or said liquid fraction to solvent-solvent extraction by adding a solvent, preferably MTHF to yield an organic phase comprising at least some of the levulinic acid, and an aqueous phase, and recovering the organic phase;
- subjecting said biomass hydrolysate or said liquid fraction or said organic phase to a first distillation to yield a first residue comprising at least 1 wt% angelica lactone, and a first distillate, and recovering said first residue;
- optionally subjecting said first distillation residue to a second distillation to yield a second distillate comprising angelica lactone and optionally levulinic acid, and a second distillation residue, and recovering said second distillate;
- subjecting said recovered first residue or said recovered second distillate to a chemical reaction step under conditions and time and temperature to produce the compound; and
- optionally isolating the compound.

The distillation residue may be used in the chemical reaction as such, or for example as a distillate of a subsequent distillation. That is, the process may comprise two or more additional, preceding distillation steps. The distillation step *stricto sensu*,

from which distillation the residue is used in the chemical reaction according to the invention, may thus be preceded by one or more distillation steps, from which either a distillate or a distillation residue is recovered in order to use in the subsequent process step.

5 The compound may be gamma valerolactone. Thus, the chemical reaction step may comprise a hydrogenation reaction resulting in gamma valerolactone. Hydrogenation of levulinic acid to produce gamma valerolactone is described in L. E. Manzer, Appl. Catal. A, 2004, 272, 249–256; J. P. Lange, J. Z. Vestering and R. J. Haan, Chem. Commun., 2007, 3488–3490; R. A. Bourne, J.G. Stevens, J.Ke and M. Poliakoff, Chem. Commun., 2007, 4632–4634; H. S. Broadbent, G. C. Campbell, W. J. Bartley and J. H. Johnson, J. Org. Chem., 1959, 24, 1847– 1854; R. V. Christian, H. D. Brown and R. M. Hixon, J. Am. Chem. Soc., 1947, 69, 1961–1963.; L.P. Kyrides and J. K. Craver, US Patent, 2368366, 1945; H. A. Schuette and R. W. Thomas, J. Am. Chem. Soc., 1930, 52, 3010–3012.

15 Suitable catalysts for the hydrogenation reaction include Ru, e.g. Ru supported on Zr oxide or Ti oxide. The amount of catalyst to be used is not critical. Preferably the amount of catalyst is between 2.5 and 2,000 ppm relative to the initial amount of levulinic acid, i.e. the amount of levulinic acid which is present in the reaction mixture at the start of the reaction when no or hardly any levulinic acid has been converted. More preferably the amount of catalyst is between 5 and 1,000 ppm, even more preferably between 10 and 500 ppm, all relative to the initial amount of levulinic acid. The hydrogenation reaction may advantageously be done at low (e.g. less than 500 ppm) catalyst concentrations whilst yielding good selectivity.

25 The temperature at which the hydrogenation reaction is carried out is not critical and may be anywhere between 100 and 250°C, more preferably between 100 and 200°C. Preferably a temperature of between 100 and 150°C is used because it seems that the highest selectivity can be obtained in this temperature range. Lower temperatures are also desired due to cost considerations and equipment requirements.

30 The pressure at which the hydrogenation reaction is carried out is also not critical, but it may be advantageous to carry out the hydrogenation reaction at lower pressure, e.g. less than 4.8 MPa. Preferably the pressure is between 1 and 4 MPa, more preferably between 1 and 3 MPa, even more preferably between 1 and 2.5 MPa, even more preferably between 1 and 2.2 MPa.

The chemical reaction step may also comprise a ketalization reaction, resulting in the production of levulinic acid ketals.

The chemical reaction step may also comprise an oxidation reaction resulting in the production of succinic acid.

5 The chemical reaction step may also comprise an amination reaction resulting in the production of delta amino levulinic acid. A suitable co-reactant includes dihydrogen.

In a further aspect the invention provides the use of reactive distillation in a process for the preparation of compound selected from the group consisting of levulinic acid ketals, gamma valerolactone, n-alkylpyrrolidones, pentandiol, pentanol, methyl
10 tetra hydrofuran, delta amino levulinic acid, and succinic acid from a composition comprising levulinic acid and optionally a compound having a boiling temperature of less than 245°C.

EXAMPLES

15 All compounds were analysed by GC.

GVL, gamma valerolactone

LA, levulinic acid

LA, angelica lactone

FA, formic acid

20 MTHF, methyl tetrahydrofuran

Example 1

100g wood chips were impregnated for 90 minutes. After impregnation, the temperature was raised to the hydrolysis temperature and the slurry was hydrolyzed in
25 the presence of approximately 5 wt% hydrosulphuric acid without stirring. After solid-liquid fractionation the liquid fraction of the resulting biomass hydrolysate was analyzed. The analysis results and the hydrolysis conditions are stated in Table 1.

Table 1

Entry	time in min	T in °C	H ₂ SO ₄ in wt%*	LA in wt%	FA in wt%	yield LA in %	yield FA in %
1	90	170	4	3.952	1.940	42.4	51.4
2	240	160	4	4.396	2.041	46.3	53.1

3	180	170	2	4.298	2.037	47.7	53.6
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* concentration on total mass (liquor + wood)

Example 2

The reaction suspension of Example 1 is cooled via evaporation of the liquid
5 reaction product. The resulting vapor is condensed resulting in a aqueous solution of
approximately 1 wt% formic acid, 0.02 wt% acetic acid and 0.02 wt% levulinic acid.

Example 3

A biomass hydrolysate was enriched with pure levulinic acid to a levulinic acid
10 concentration of 9.07 wt%, and with formic acid to a formic acid concentration of 1.89
wt%, in order to simulate the flash step in Example 2. A total of 2.1 kg enriched
biomass hydrolysate was extracted 5 times with each time 1.7kg of fresh
methyltetrahydrofuran at 60°C. After the fifth extraction 99.1 wt% of the levulinic acid
and 98.8 wt% of the formic acid present in the reaction solution could be collected in
15 the organic layer.

Example 4

Nine kg of the collected organic layer from the extraction described above was
batch wise distilled. The initial concentrations were: levulinic acid, 1.74wt%; formic acid,
20 0.33 wt%; acetic acid, 0.1 wt%. The organic phase was distilled to remove the
extraction solvent with a falling film evaporator in a 3m BX column with a diameter of
7cm at 500mbar with a reflux ratio of 2. Eight kg of distillate was collected containing
MTHF and water, and trace levels of formic acid, acetic acid and levulinic acid (all
below 100 ppm). One kg of distillation residue was found to contain 92 wt% of the
25 levulinic acid feed, and 100 wt% of the formic acid feed, respectively.

Example 5

The residue of the distillation of Example 4 is subjected to a further distillation to
remove any low boiling compounds, the decreasing the pressure from 500mbar to
30 20mbar and increasing the temperature from 125°C to 175°C. The first fraction contains
(nearly) pure methyltetrahydrofuran. The second fraction contains 75 wt%
methyltetrahydrofuran and 20 wt% formic acid. The third fraction (bottom temp, 142°C)

contains 20 wt% methyltetrahydrofuran, 65 wt% formic acid and 8 wt% acetic acid. No fraction can be isolated containing any detectable amounts of levulinic acid. Instead, the distillation residue is rich in levulinic acid and angelica lactone, and contains no detectable amounts of formic acid or acetic acid.

5

Example 6

A residue of a distillation as described in Example 5 which rich in angelica lactone and levulinic acid is subjected to a further distillation to remove any high boiling substances such as humins. This distillation yields a distillate containing angelica lactone and levulinic acid, and contains no detectable amounts of other compounds.

10

Example 7

A distillation residue according to Example 5 was distilled. Two distillate fractions were recovered both containing (nearly) pure angelica lactone. Of the feed to the distillation, 5 wt% ended up as the residue. The amount of angelica lactone in the collected distillates corresponded to 95 mol% relative to the amount of the levulinic acid present in the feed.

15

Example 8

In a stirred stainless steel autoclave with continuous hydrogen supply, 2.5 g of a solution containing levulinic acid and angelica lactone (see Table 2) was contacted with a 1 % wt Ru/C catalyst (1.25mg Ru, Escat 440) at 100°C and a hydrogen pressure of 25 bar for 16h. The reaction mixture was analyzed and the results are stated in Table 2.

20

Table 2

25

Entry	Ratio AL:LA	Conversion AL	Yield GVL (%)
4	9:1	100	75.1
5	4:1	100	71.9
6	6.5:3.5	100	66.9
7	1:1	100	57.2

Example 9

In a stirred stainless steel autoclave with continuous hydrogen supply angelica lactone (2.7g) was contacted with a 5%wt Ru/C catalyst (70mg Ru) at elevated temperature (150°C) and hydrogen pressure (25 bar) for 16h. The reaction mixture was analyzed and contained 2.4g g-valerolactone representing a g-valerolactone yield of 86%.

Example 10

In a stirred stainless steel autoclave with continuous hydrogen supply angelica lactone (2g) and water (2g) were contacted with a 5%wt Ru/C catalyst (100mg Ru) at elevated temperature (150°C) and hydrogen pressure (25 bar) for 16h. The reaction mixture was analyzed and the reaction contained 2g water and 2.0g GVL representing a GVL yield of 95%.

CLAIMS

1. Process for the preparation of a compound selected from the group consisting of levulinic acid ketals, gamma valerolactone, n-alkylpyrrolidones, pentandiol, 5 pentanols, methyl tetra hydrofuran, delta amino levulinic acid, and succinic acid from a composition comprising levulinic acid and optionally a compound having a boiling temperature of less than 245°C said process comprising:
 - subjecting the composition to distillation and recovering a residue comprising at least 1 wt% angelica lactone;
 - 10 - subjecting the recovered residue to a chemical reaction step under conditions and time and temperature to produce the compound; and optionally
 - isolating the compound.
2. Process according to claim 1 wherein the compound is gamma valerolactone.
- 15 3. Process according to claim 1 or 2 wherein the composition comprises formic acid, acetic acid, furfural, and/or propionic acid.
4. Process according to any one of claim 1 - 3 wherein the composition comprises a biomass hydrolysate.
5. Process according to claim 4 wherein said biomass hydrolysate is made by acid 20 hydrolysis of lignocellulosic biomass.
6. Process according to any one of claim 1 - 3 wherein the composition is made by acid hydrolysis of fructose or glucose or a combination thereof.
7. Process according to any one of claim 1-6 wherein the process is carried out as a batch process.
- 25 8. Process according to any one of claim 1-7 where the distillation comprises reactive distillation.
9. Use of reactive distillation in a process for the preparation of compound selected from the group consisting of levulinic acid ketals, gamma valerolactone, n-alkylpyrrolidones, pentandiol, pentanols, methyl tetra hydrofuran, delta amino 30 levulinic acid, and succinic acid from a composition comprising levulinic acid and optionally a compound having a boiling temperature of less than 245°C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2013/075960

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-8

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D307/33 B01D3/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98/19986 A1 (ARKENOL INC.) 14 May 1998 (1998-05-14) page 8, line 14 - line 22 ----- -/--	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/075960

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	----- US 2005/171374 A1 (MANZER LEO E [US]) 4 August 2005 (2005-08-04) example 62 page 6, paragraph 0090 - page 7, paragraph 0098 paragraph [0087]	1-8
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Y	----- CHEON PARK ET AL: "Palladium Nanoparticles in Polymers: Catalyst for Alkene Hydrogenation, Carbon-Carbon Cross-Coupling Reactions, and Aerobic Alcohol Oxidation", SYNTHESIS, vol. 2006, no. 22, 1 November 2006 (2006-11-01), pages 3790-3794, XP055050937, ISSN: 0039-7881, DOI: 10.1055/s-2006-950329 table 3 ----- -/--	1-8

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KIM N ET AL: "One-pot synthesis of recyclable palladium catalysts for hydrogenations and carbon-carbon coupling reactions", TETRAHEDRON LETTERS, ELSEVIER, AMSTERDAM, NL, vol. 45, no. 38, 13 September 2004 (2004-09-13), pages 7057-7059, XP004546660, ISSN: 0040-4039, DOI: 10.1016/J.TETLET.2004.07.126 table 3 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/075960

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GB 1596651	A	26-08-1981	NONE

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8

Process according to claim 1

2. claim: 9(partially)

Use of reactive distillation in a process for the preparation of LA ketals from a composition comprising LA

3. claim: 9(partially)

Use of reactive distillation in a process for the preparation of GVL from a composition comprising LA

4. claim: 9(partially)

Use of reactive distillation in a process for the preparation of n-alkylpyrrolidones from a composition comprising LA

5. claim: 9(partially)

Use of reactive distillation in a process for the preparation of pentandiols from a composition comprising LA

6. claim: 9(partially)

Use of reactive distillation in a process for the preparation of pentanols from a composition comprising LA

7. claim: 9(partially)

Use of reactive distillation in a process for the preparation of MTHF from a composition comprising LA

8. claim: 9(partially)

Use of reactive distillation in a process for the preparation of delta amino LA from a composition comprising LA

9. claim: 9(partially)

Use of reactive distillation in a process for the

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

preparation of succinic acid from a composition comprising
LA
